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(54) **HYDROXY CONTAINING FLUOROVINYL COMPOUNDS AND POLYMERS THEREOF.**

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Description

A process for reducing ester containing fluorovinyl compounds to the corresponding alcohol with alkali metal borohydrides, selected novel hydroxy containing fluorovinyl ethers, novel polymers of hydroxy containing fluorovinyl ethers, a process for making such polymers and novel copolymers of selected hydroxy containing fluorovinyl ethers are provided.

BACKGROUND OF THE INVENTION

Japanese Patent 88002418 reports the synthesis of 7,7-dihydro-7-hydroxy(perfluoro-3-oxahepten-1) by chlorinating the methyl ester of perfluoro(3-oxa-1-heptenoic acid), reduction of the chlorinated product with $NaBH_4$ to give the corresponding alcohol, and then reaction of the alcohol with zinc metal to regenerate the vinyl ether, which is the desired product. It is reported that this compound can be free radically copolymerized with at least one other fluorinated monomer, and optionally non-fluroinated monomers, to form useful polymers.

U. S. Patent 4,564,717 reports the synthesis of compounds of the formula $CF_2=CF(CF_2)_m(CH_2)_nOH$ wherein m is an integer from 0 to 10 and n is an integer of 1 to 4. Among the methods of preparation described, is the reduction of the compound $CF_2X^1CFX^2CF_2COOR$ (sic) wherein R is alkyl and X^1 and X^2 are chlorine or bromine, by various reducing agents including alkali metal borohydrides. The olefin is then produced by dehalogenation of the alcohol with a metal such as zinc. In essence, in both this and the previous reference, the double bond has been "protected" by halogenating it (with chlorine or bromine) before the reduction step, and dehalogenating after the reduction step.

European Patent Application 135,917 discloses copolymers of vinylidene fluoride with a compound of the formula $CF_2=CF(CF_2)_m(CH_2)_nOH$ where m is 0 to 10 and n is 1-4, and optionally another fluorinated termonomer. Polymers of hydroxy containing fluorovinyl ethers are not mentioned.

European Patent Application 199,138 reports preparation and polymerization (with other fluorine containing olefins) of the compound $CF_2=CFO(CF_2CFYO)_n(CF_2CF_2CH_2O)_mCF_2CF_2CH_2X$, wherein X is hydrogen or halogen, Y is fluorine or $-CF_3$, m is an integer of 0 to 5 and n is 0, 1 or 2. No mention is made of a hydroxy group being present.

It is one object of the present invention to provide a simplified method for the production of hydroxy containing fluorovinyl compounds by the alkali metal borohydride reduction on the corresponding esters. It is an additional object to conduct the reduction process so protection of the double bond, as by halogenation, is unnecessary.

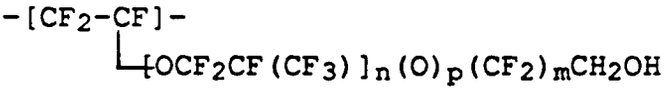
A further object of the invention is to homopolymerize hydroxy containing fluorovinyl ethers using anionic catalysts. It is an additional object to disclose polymers resulting from the polymerization of hydroxy containing fluorovinyl ethers.

Finally, it is also an objective of this invention to provide certain novel hydroxy containing fluorovinyl ethers and their copolymers with selected monomers.

These and other objects are achieved by the invention disclosed in the below specification and in the appended claims.

SUMMARY OF THE INVENTION

This invention concerns a process for the production of hydroxy containing fluorovinyl compounds, comprising, contacting in a solvent an alkali metal borohydride with a compound of the formula $CF_2=CFR^1CO_2R^2$ wherein R^1 is a covalent bond, a perfluoroalkylene group and $-OR^3-$ wherein R^3 is a perfluoroalkylene group, and R^2 is hydrocarbyl or substituted hydrocarbyl. This invention further concerns hydroxy containing fluorovinyl ethers of the formula $CF_2=CF[OCF_2CF(CF_3)]_n(O)_p(CF_2)_mCH_2OH$ wherein p is 0 or 1, m is 0 to 10 and n is 1 to 20, provided that when m is 0, p is 0, and further provided that when m is greater than 0, p is 1. Also disclosed is a process for polymerizing hydroxy containing fluorovinyl ethers, comprising, contacting a base with one or more hydroxy fluorovinyl ethers of the formula $CF_2=CFOR^4CF_2CH_2OH$, wherein R^4 is perfluoroalkylene. A polymer consisting essentially of the repeat formula $-[CF_2CFHOR^4CF_2CH_2O]-$, wherein R^4 is perfluoroalkylene. Also disclosed is a copolymer containing the hydroxy containing repeat unit



wherein p is 0 or 1, m is 0 to 10 and n is 1 to 20, provided that when m is 0, p is 0, and further provided that when m is greater than 0, p is 1, with other selected repeat units.

DETAILS OF THE INVENTION

In accordance with the present invention, there is provided a process for the production of hydroxy containing fluorovinyl compounds, comprising, contacting in a solvent an alkali metal borohydride with a compound of the formula $CF_2=CFR^1CO_2R^2$ wherein R^1 is selected from a covalent bond, a perfluoroalkylene group and $-OR^3-$wherein R^3 is a perfluoroalkylene group, and R^2 is hydrocarbyl or substituted hydrocarbyl.

By "perfluoroalkylene group" herein is meant a bivalent saturated radical regarded as derived from a perfluorinated alkane by the removal of two fluorine atoms from different carbon atoms. The "perfluoroalkylene group" may also contain oxygen atoms between alkylene segments, to form one or more ether groups in each perfluoroalkylene group.

By "substituted hydrocarbyl" herein is meant any substituent in a hydrocarbyl group that will not interfere with the reduction reaction. However, even substituents that react with the alkali metal borohydrides may be present, provided enough borohydride is added to reduce the ester to the alcohol.

Preferred alkali metal borohydrides are lithium borohydride, sodium borohydride and potassium borohydride. The molar ratio of borohydride to ester is 0.3 to 1.2, preferably 0.4 to 0.8.

It is preferred that the solvent is an alcohol. Preferred alcohols are methanol and ethanol.

The process is carried out at -10 to +30 °C, preferably 0 to 15 °C and most preferably 5 to 10 °C. External cooling may be needed to maintain the correct temperature.

Any substantial amount of water should be excluded from the reaction, and it is convenient to carry out the reaction under an inert atmosphere such as nitrogen, in order to exclude moisture. Starting materials should be substantially dry. Agitation is preferred during the reaction, and it is preferred if the agitation is vigorous for efficient mixing.

Products may be isolated by standard techniques well known to those skilled in the art, such as distillation. Such techniques are illustrated in the Examples.

Typical procedures for preparing compounds of the formula $CF_2=CFR^1CO_2R^2$ are found U. S. Patent 4,275,226; R. Sullivan in J. Org. Chem., vol. 34, pp. 1841-1844 (1969); U. S. Patent 4,281,092; and U. S. Patent 4,138,426.

In preferred embodiments R^1 is $-OR^3-$, wherein R^3 is $-(CF_2)_y-$, wherein y is 2 to 10; or R^1 is $-OR^3-$ wherein R^3 is $-[CF_2CF(CF_3)O]_x(CF_2)_z-$, wherein z is 1 to 10 and x is 1 to 20; or R^1 is perfluoroalkylene; or R^1 is a covalent bond. In an especially preferred embodiments R^1 is $-(CF_2)_q-$ wherein q is 1 to 10; or x is 1 and z is 2. In a preferred embodiment of the process R^2 is alkyl, and it is especially preferred if R^2 is alkyl in combination with any of the preferred embodiments of R^1. Unless otherwise noted, all numerical ranges that refer to chemical formulas herein, represent integers throughout those particular ranges, and not fractional values.

The hydroxy containing fluorovinyl compounds produced by the above process are useful as monomers in polymerization, and may be homo- or copolymerized (infra).

Also disclosed are hydroxy containing fluorovinyl ethers of the formula $CF_2=CF[OCF_2CF(CF_3)]_n(O)_p-(CF_2)_mCH_2OH$ wherein p is 0 or 1, m is 0 to 10 and n is 1 to 20, provided that when m is 0, p is 0, and further provided that when m is greater than 0, p is 1.

In a preferred embodiment of the hydroxy containing fluorovinyl ethers n is 1 to 5, p is 1 and m is 2 to 10. In the most preferred embodiment n is 1, p is 1 and m is 2.

Also disclosed is a process for polymerizing hydroxy containing fluorovinyl ethers, comprising, contacting a base with one or more hydroxy fluorovinyl ethers of the formula $CF_2=CFOR^4CF_2CH_2OH$, wherein R^4 is perfluoroalkylene.

The polymers produced by this process are described below.

The polymerization process is preferably carried out in a solvent, preferably a polar but nonprotic solvent. Such solvents are well known to those skilled in the art, and include, but are not limited to N,N-dimethylformamide, dimethylsulfoxide, N,N-dimethylacetamide, tetrahydrofuran, the glymes, etc. N,N-dimethylformamide is preferred. Protic solvents, particularly those that contain a proton more acidic than the

hydroxy group in the hydroxy containing fluorovinyl ethers should be avoided. The solvents, and indeed all starting materials should be substantially free of water.

The base used in the process should be one whose conjugate acid is less acidic than the hydroxy proton in the hydroxy containing fluorovinyl ether. The base should also be at least slightly soluble in the reaction medium, so that reaction may be affected. Such bases are well known to those skilled in the art, and include, but are not limited to alkali metal alkoxides, alkali metal hydrides, amines, etc. Alkali metal alkoxides are preferred, and potassium t-butoxide is especially preferred. The molar ratio of hydroxy containing fluorovinyl ether to base is 5 to 100, preferably 8 to 50, most preferably 10 to 25.

The process is run at a temperature of -10 ° to +100 ° C, preferably 0 ° to 50 ° C, most preferably 10 ° to 30 ° C. Agitation of the reaction mass is preferred to mix separate phases.

The product polymers may be isolated by techniques well known to those skilled in the art, such as evaporation of solvent. Such techniques are illustrated in the Examples.

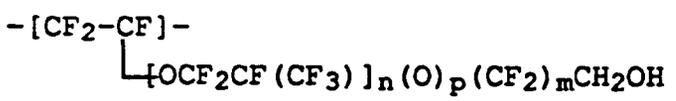
In preferred hydroxy containing fluorovinyl ethers used in the process R^4 is $-(CF_2)_s-$, wherein s is 1 to 10; or R^4 is $-[CF_2CF(CF_3)O]_t(CF_2)_u-$, wherein u is 1 to 10 and t is 1 to 20. In an especially preferred embodiment t is 1 and u is 1, or s is 2.

A polymer consisting essentially of the repeat formula $-[CF_2CFHOR^4CF_2CH_2O]-$, wherein R^4 is perfluoroalkylene.

In preferred polymers R^4 is $-(CF_2)_s-$, wherein s is 1 to 10; or R^4 is $-[CF_2CF(CF_3)O]_t(CF_2)_u-$, wherein u is 1 to 10 and t is 1 to 20. In an especially preferred embodiment t is 1 and u is 1, or s is 2.

These polymers are useful as lubricants, lubricant precursors, macromonomers and coatings. These polymers are made by the process described immediately above.

A copolymer comprising the hydroxy containing repeat unit



wherein p is 0 or 1, m is 0 to 10 and n is 1 to 20, provided that when m is 0, p is 0, and further provided that when m is greater than 0, p is 1, and one or more other repeat units.

Such a repeat unit, which has a hydroxy contained within it, is useful as a reactive site along the polymer chain to accomplish processes such as crosslinking, or may change the surface characteristics of a polymer while leaving the bulk properties relatively unchanged. Thus in many cases the above repeat unit will be present in the polymer in only relatively small amounts, 0.001 to 30 mole percent, preferably 0.05 to 15 mole percent.

It is especially useful in crosslinking relatively unreactive polymers, such as fluoropolymers. Thus it can be incorporated into polymers containing repeat units derived from monomers selected from the group consisting of tetrafluoroethylene; hexafluoropropylene and vinylidene fluoride; hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene; ethylene and vinylidene fluoride; perfluoro(methyl vinyl ether) and tetrafluoroethylene; perfluoro(methyl vinyl ether) and hexafluoropropylene; chlorotrifluoroethylene; ethylene and chlorotrifluoroethylene; vinylidene fluoride; tetrafluoroethylene and propylene; tetrafluoroethylene and ethylene; tetrafluoroethylene and hexafluoropropylene; perfluoro-2,2-dimethyl-1,3-dioxole; perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene; vinyl fluoride; tetrafluoroethylene and perfluoro[2-(fluorosulfonylethoxy)propyl vinyl ether]; and vinyl acetate and tetrafluoroethylene. In the immediately above listing of monomers, each of the monomer(s) between the semicolons represents a specific copolymer of the hydroxy containing fluorovinyl ether with that particular monomer or combination of monomers. By "incorporated into polymers" in the sentence above is meant that when the above polymers (and others not specifically mentioned) are formed by free radical polymerization, the appropriate amount of hydroxy containing fluorovinyl ether monomer is added to the polymerization reaction to be copolymerized with the other monomer(s). It will be noted that the polymers above contain fluoromonomers. The term fluoromonomers means a monomer containing a vinyl group to which at least 1 fluorine atom is directly bound (i.e. has one or more vinylic fluorine atoms). Copolymers of the hydroxy containing fluorovinyl ethers with fluoromonomers, and optionally other monomers, are preferred. Also preferred are copolymers with vinyl esters, and especially preferred is vinyl acetate. Such polymers are useful for example, as molding resins (when plastic) and elastomers (where the "base" polymer is an elastomer).

These copolymers can be made by methods well known to those skilled in the art. Further illustrations of typical polymerizations processes are given in the Examples.

In the following Examples, the following abbreviations and terms are used:
t-BuOK - potassium t-butoxide
dispersion factor - weight average molecular weight/number average molecular weight
DMF - N,N-dimethylformamide
DSC - differential scanning calorimetry
EtOH - ethanol
EVE - methyl perfluoro(4,7-dioxa-5-methylhept-8-enoate)
EVE alcohol - perfluoro(9,9-dihydro-9-hydroxy-3,6-dioxa-5-methylnon-1-ene)
F-113 - 1,1,2-trichloro-1,2,2-trifluoroethane
GPC - gel permeation chromatorgraphy
PDD - perfluoro(2,2-dimethyl-1,3-dioxole) (Can be made by methods described in U.S. Patents 3,865,845, 3,978,030 and 4,393,227)
PMMA - poly(methyl methacrylate)
TFE - tetrafluoroethylene
Tg - glass transition temperature
Tm - melting temperature
VAc - vinyl acetate

EXAMPLE 1

Preparation of 9,9-Dihydro-9-hydroxy-perfluoro-(3,6-dioxa-5-methyl-1-nonene)($CF_2=CFO-CF_2CF(CF_3)O-CF_2CF_2-CH_2OH$):

To a dry flask was charged EVE (211 g, 0.50 mole) in absolute ethanol (300 ml) with a magnetic stirring bar. Sodium borohydride (11.34 g, 0.30 mole) was added slowly from a solid addition funnel. The reaction was somewhat exothermic and the reaction pot was kept at ≦ 10 °C by external cooling. After the addition of sodium borohydride was completed, the reaction mixture was stirred for 1 hr at room temperature. The pot mixture was then dumped into an ice water (600 ml)/6N HCl (600 ml) mixture. The bottom product layer was separated, washed with water and distilled to give the desired product as a clear, colorless liquid. Bp. 68 °C/25 mmHg. Yield: 168.7 g (85.6 %). H-1 NMR($CDCl_3$): 4.00 (dt, J = 1.0 Hz, 13.5 Hz, 2H), 2.12 (s, br, 1H); F-19 NMR ($CDCl_3$, F-11 internal standard): -80.4 (s, br, 3F), -84.2 (s, br, 2F), -85.3 (m, br, 2F), -126.6 (t, J = 14 Hz, 2F), -145.7 (t, J = 21.8 Hz, 1F), -113.4, -113.7, -113.8, -114.2 (4s, 1F), -121.6, -112.1, -122.2, -122.7 (4t, J = 5.2 Hz, 1F), -135.3, -135.6, -135.9, -136.2 (4t, J = 5.8 Hz, 1F).

EXAMPLE 2

Preparation of 9,9-Dihydro-9-hydroxyperfluoro-(3,6-dioxa-5-methyl-1-nonene)

EVE (21.1 g, 0.05 mole) was dissolved in absolute ethanol (15 ml) at 0 °C. In a separate flask was charged sodium borohydride (1.15 g, 0.03 mole) in absolute ethanol (20 ml) at 0 °C. The $NaBH_4$/EtOH solution was added slowly into EVE/EtOH solution while the pot temperature was kept between 0 to 5 °C. After addition, the reaction mixture was stirred for 15 min at room temperature. The product was worked up as described in Example 1 and distilled to give the clear, colorless product 11.7 g (59.4% yield) as a liquid. Bp. 70 °C/25 mmHg.

EXAMPLE 3

Preparation of 7,7-Dihydro-7-Hydroxyperfluoro(3-Oxa-1-Heptene)($CF_2=CFO-CF_2CF_2CF_2-CH_2OH$):

To a dry flask was charged methyl perfluoro (5-oxa-6-heptenoate) (61.2 g, 0.2 mole) in absolute ethanol (120 ml). Sodium borohydride (4.54 g, 0.12 mole) was added slowly into the reaction solution via a solid additional funnel while the temperature was kept at about 10 °C. The mixture was allowed to stir at room temperature for 1 hr after the addition of $NaBH_4$ was completed. The mixture was then dumped into ice water/6NHCl (1:1 v/v, 500 ml) and worked up. The product was isolated by final distillation. 47.6 g (85.6% yield) of the desired product was obtained as a clear, colorless liquid. Bp. 54-55 °C/30 mmHg. H-1 NMR ($CDCl_3$): 4.10 (t, J = 14.5 Hz, 2H); 2.65 (s, br, 1H); F-19 NMR (188.24 MHz, $CDCl_3$): -85.7 (m, 2F), -123.4 (m, 2F), -127.6 (s, br, 2F), -113.7, -114.1, -114.2, -114.5 (4m, 1F), -121.8, -122.3, -122.4, -122.9 (4t, J = 5.6 Hz, 1F), -134.9, -135.2, -135.5, -135.8 (4t, J = 5.6 Hz, 1F).

EXAMPLE 4

Homopolymerization of $CF_2=CFO-CF_2CF(CF_3)O-CF_2CF_2-CH_2OH$:

Potassium t-butoxide (0.112 g, 0.001 mole) was dissolved in N,N-dimethyl formamide(DMF) (10 ml) and was cooled to 0 °C. The title vinyl ether alcohol (7.88 g, 0.02 mole) in DMF (4 ml) was added slowly into the above solution via syringe. The reaction was maintained between at 10 to 25 °C via external cooling. After the addition was finished, the mixture was stirred for 2 hrs at about 10 °C, then warmed up gradually to room temperature and was continued at ambient temperature for 6 hrs. The product mixture was dumped into ice water and was extracted with ether. The ether layer was separated, washed thoroughly with water and dried over magnesium sulfate. Ether solvent was removed in vacuo and the product polymer was further dried under high vacuum. 4.24 g (53.8 % yield) of polymeric viscous oil was obtained. The weight average molecular weight was determined to be 4,100 with dispersion factor 1.51 by GPC with PMMA as the reference standard. The structure of the product was supported by its H-1 and F-19 NMR spectroscopic data.

EXAMPLE 5

Homopolymerization of $CF_2=CFO-CF_2CF(CF_3)O-CF_2CF_2-CH_2OH$:

The title vinyl ether alcohol (7.88 g, 0.02 mole) was polymerized with potassium t-butoxide (0.112 g, 0.001 mole) in DMF as described in Example 4. After warmed to room temperature, the reaction mixture was stirred at ambient temperature for 48 hrs instead of 6 hrs. After working up, the polymeric oil was determined to have weight average molecular weight 5,920 with a dispersion factor 1.74 by GPC with PMMA as reference standard.

EXAMPLE 6

Homopolymerization of $CF_2=CFO-CF_2CF_2CF_2-CH_2OH$:

Potassium t-butoxide (0.112 g, 0.001 mole) was dissolved in DMF (10 ml) at 10 °C. The alcohol substrate (5.56 g, 0.02 mole) in DMF (4 ml) was added slowly into the t-BuOK/DMF solution slowly via syringe. After stirring for 2 hrs at 10 °C, the reaction mixture was warmed slowly to room temperature. Some exotherm was observed when temperature reached 25 °C. The reaction mixture was cooled and kept stirring for 6 hrs at room temperature. The product was then dumped into ice water and was worked up as previously described. 4.13 g (74.3 % yield) of pale-yellow viscous polymeric oil was obtained. The weight average molecular weight of this polymer was determined to be 4,970 with dispersion factor 2.00 by GPC by the use of PMMA as the reference standard.

EXAMPLE 7

Free Radical Copolymerization of EVE Alochol with TFE:

In a shaker tube was charged EVE Alcohol (10 g, 0.0254 mole), 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) (60 g, 0.32 mole) and 4,4'-bis(t-butylcyclohexyl)peroxy dicarbonate (0.05 g). The tube was sealed, cool-evacuated and tetrafluoroethylene (10 g, 0.1 mole) was then charged. The tube was sealed again and was heated at 50 °C, 60 °C and 70 °C for 2 hrs respectively with shaking. The solvent was removed from the unloaded polymer solution and the polymer was finally dried in a vacuum oven (ca. 150 mmHg) at 120 °C for 24 hrs. White polymer, 9.0 g, was obtained. The polymer has a Tm at 240 °C as measured by DSC. The composition of this polymer was determined to be TFE/EVE alcohol = 87/13 (mole %) by F-19 high temperature NMR spectroscopy.

EXAMPLE 8

Free Radical Copolymerization of EVE Alcohol with TFE:

In the shaker tube was charged EVE alcohol (10 g, 0.0254 mole), F-113 solvent (20 g, 0.107 mole) and 4,4'-bis(t-butylcyclohexyl)peroxy dicarbonate (0.03 g). The tube was sealed and cool-evacuated and

tetrafluoroethylene was charged in. The tube was heated to 45 °C and the pressure of tetrafluoroethylene maintained at 60 psi. The tube was shaken for 6 hrs and was worked up as in Example 7. 3.3 g of the white polymer was obtained. This polymer has shown a Tg at 164 °C as determined by DSC, and have a composition of TFE/EVE alcohol = 74/26 (mole %) as determined by F-19 high temperature NMR spectroscopy.

EXAMPLE 9

Free Radical Copolymerization of EVE Alcohol and TFE:

This polymerization was carried out with EVE alcohol monomer (4 g, 0.0102 mole), F-113 (72 g, 0.417mole), 4,4'-bis(t-butylcyclohexyl)peroxy dicarbonate (0.05 g) and tetrafluoroethylene (20 g, 0.2 mole) in a shaker tube at 50 °C, 2 hrs; 60 °C, 2 hrs and 70 °C, 2 hrs. 17.3 g of white polymer was obtained. The polymer has a Tm at 318.3 °C as shown by DSC and has a composition of EVE alcohol 98.5-99.0/1.5-1.0 (mole %) as determined by F-19 NMR.

EXAMPLE 10

Free Radical Copolymerization of EVE Alcohol and PDD:

This polymerization was carried out with EVE alcohol (5 g, 0.0127 mole) and PDD (30 g, 0.123 mole) in F-113 (100 g, 0.533 mole) with 4,4'-bis(t-butylcyclohexyl)peroxy dicarbonate (0.06 g) initiator under the same temperature as described in Example 9. White polymer 6.3 g was obtained after workup. This polymer has a Tg at 210 °C. The composition of this polymer was determined to be PDD/EVE alcohol = 96.5/3.5, (mole %) by F-19 NMR.

EXAMPLE 11

Free Radical Copolymerization of EVE Alcohol, TFE and VAc

In the shaker tube was charged EVE alcohol (10 g, 0.0254 mole), VAc (40 g, 0.465 mole), F-113 (120 g, 0.64 mole) and 4,4'-bis(t-butylcyclohexyl)peroxy dicarbonate (0.1 g). The tube was sealed and tetrafluoroethylene (4 g, 0.04 mole) was added after the tube was cooled and evacuated. The tube was resealed and was heated at 60 °C for 6 hrs. The resulting polymer solution was dissolved in acetone and precipitated with ice water. The polymer was collected by filtration and washed with water and was dried under nitrogen purge at ambient temperature. White solid polymer 48.7 g was obtained. The polymer has a Tg at 40.6 °C by DSC and the polymer has a composition of VAc/TFE/EVE alcohol = 62.8/27.6/9.6 (mole %) as calculated from its H-1 & F-19 NMR spectroscopic data. The structure of the polymer was also supported by its IR spectrum.

EXAMPLE 12

Free Radical Copolymerization of EVE Alcohol, TFE and PDD

This experiment was carried out with EVE alcohol (2 g, 0.0051 mole), PDD (51 g, 0.209 mole) and tetrafluoroethylene (1 g, 0.01 mole) in F-113 (165 g, 0.88 mole) by the use of 4,4'-bis(t-butylcyclohexyl)-peroxy dicarbonate initiator (0.2 g) in a shaker tube at 50 °C, 60 °C and 70 °C for 2 hrs respectively. 44.9 g of white polymer was obtained after working up. This polymer has shown a Tg at 224.3 °C by DSC.

Claims

1. A process for the production of hydroxy containing fluorovinyl compounds, comprising, contacting in a solvent an alkali metal borohydride with a compound of the formula $CF_2 = CFR^1CO_2R^2$

wherein:

R^1 is selected from a covalent bond, a perfluoroalkylene group and $-OR^3-$;

R^2 is hydrocarbyl or substituted hydrocarbyl; and

R^3 is a perfluoroalkylene group,

wherein in R^1 and R^3 "perfluoroalkylene group" is a bivalent saturated radical derived from a

perfluorinated alkane by the removal of two fluorine atoms from different carbon atoms and which, optionally, contains oxygen atoms between segments, to form one or more ether groups in each perfluoroalkylene group.

2. The process as recited in Claim 1 wherein said solvent is an alcohol.

3. The process as recited in Claim 2 wherein said alcohol is selected from the group consisting of ethanol and methanol.

4. The process as recited in Claim 1 or Claim 2 wherein the temperature is -10 ° to +30 ° C.

5. The process as recited in Claim 4 wherein said temperature is 0 ° to 15 ° C.

6. The process as recited in Claim 5 wherein said temperature is 5 ° to 10 ° C.

7. The process as recited in Claim 1 or Claim 2 wherein the molar ratio of said borohydride to said compound is 0.3 to about 1.2.

8. The process as recited in Claim 7 wherein said molar ratio is 0.4 to 0.8.

9. The process as recited in Claim 1 or Claim 2 wherein the reaction mass is agitated.

10. The process as recited in Claim 1 wherein said R^1 is $-OR^3-$, wherein R^3 is $-(CF_2)_y-$, wherein y is 2 to 10.

11. The process as recited in Claim 1 wherein said R^1 is $-OR^3-$, wherein R^3 is $-[CF_2CF(CF_3)O]_x(CF_2)_z-$, wherein z is 1 to 10, and x is 1 to 20.

12. The process as recited in Claim 11 wherein said x is 1 and said z is 2.

13. The process as recited in Claim 1 wherein said R^1 is perfluoroalkylene.

14. The process as recited in Claim 13 wherein said R^1 is $-(CF_2)_q-$, wherein q is 1 to 10.

15. The process as recited in Claim 1 wherein said R^1 is a covalent bond.

16. The process as recited in Claim 1 or Claim 2 or Claim 10, or Claim 11 or Claim 12 or Claim 13, or Claim 14 or Claim 15, wherein said R^2 is alkyl.

17. The process as recited in Claim 1 or Claim 2 wherein said alkali metal borohydride is selected from the group consisting of lithium borohydride, sodium borohydride and potassium borohydride.

18. The process as recited in Claim 7 wherein the temperature is -10 to +30 ° C.

19. Hydroxy containing fluorovinyl ethers of the formula $CF_2=CF[OCF_2CF(CF_3)]_n(O)_p(CF_2)_mCH_2OH$ wherein:

p is 0 or 1;

m is 0 to 10 and n is 1 to 20; and provided that when m is 0, p is 0; and further provided that when m is greater than 0, p is 1.

20. The ethers as recited in Claim 19 wherein:

n is 1 to 5;

p is 1; and

m is 2 to 10.

21. The ethers as recited in Claim 19 wherein:

n is 1;

p is 1; and

m is 2.

22. A process for polymerizing hydroxy containing fluorovinyl ethers, comprising, contacting a base with one or more hydroxy fluorovinyl ethers of the formula $CF_2=CFOR^4CF_2CH_2OH$, wherein R^4 is perfluoroalkylene.

23. The process as recited in Claim 22 carried out in a solvent.

24. The process as recited in Claim 23 wherein said solvent is a polar, nonprotic solvent.

25. The process as recited in Claim 24 wherein said solvent is selected from the group consisting of N,N-dimethylformamide, dimethylsulfoxide, N,N-dimethylacetamide and tetrahydrofuran.

26. The process as recited in Claim 25 wherein said solvent is N,N-dimethylformamide.

27. The process as recited in Claim 22 or Claim 24 wherein said base is selected from the group consisting of alkali metal alkoxides, alkali metal hydrides and amines.

28. The process as recited in Claim 27 wherein said base is an alkali metal alkoxide.

29. The process as recited in Claim 28 wherein said alkali metal alkoxide is potassium t-butoxide.

30. The process as recited in Claim 22 or Claim 24 wherein the temperature is -10° to +100°C.

31. The process as recited in Claim 30 wherein said temperature is 0° to 50°C.

32. The process as recited in Claim 31 wherein said temperature is 10° to 30°C.

33. The process as recited in Claim 22, Claim 24 or Claim 27 wherein the molar ratio of said hydroxy containing fluorovinyl ether to said base is 5 to 100.

34. The process as recited in Claim 33 wherein said molar ratio is 8 to 50.

35. The process as recited in Claim 34 wherein said molar ratio is 10 to 25.

36. The process as recited in Claim 22 or Claim 24 wherein the reaction mass is agitated.

37. The process as recited in Claim 24 wherein said R^4 is $-(CF_2)_s-$, wherein s is 1 to 10.

38. The process as recited in Claim 37 wherein said s is 2.

39. The process as recited in Claim 24 wherein said R^4 is $-[CF_2CF(CF_3)O]_t(CF_2)_u-$, wherein u is 1 to 10, and t is 1 to 20.

40. The process as recited in Claim 39 wherein said t is 1 and said u is 1.

41. The process as recited in Claim 37 or Claim 39 wherein the temperature is -10° to +100°C.

42. The process as recited in Claim 40 or Claim 41 wherein the molar ratio of said hydroxy containing fluorovinyl ether to said base is 5 to 100.

43. The process as recited in Claim 42 wherein said base is an alkali metal alkoxide.

44. A polymer consisting essentially of the repeat formula $-[CF_2CFHOR^4CF_2CH_2O]-$, wherein R^4 is perfluoroalkylene.

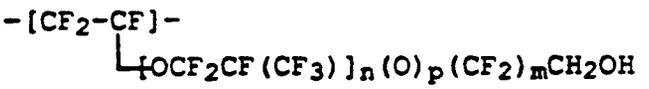
45. A polymer as recited in Claim 44 wherein said R^4 is $-(CF_2)_s-$, wherein s is 1 to 10.

46. The polymer as recited in Claim 45 wherein said s is 2.

47. A polymer as recited in Claim 44 wherein said R^4 is $-[CF_2CF(CF_3)O]_t(CF_2)_u-$ wherein t is 1 to 20, and u is 1 to 10.

48. A polymer as recited in Claim 47 wherein said t is 1 and said u is 1.

49. A copolymer comprising the hydroxy containing repeat unit



wherein:

p is 0 or 1;
m is 0 to 10; and
n is 1 to 20;
provided that when m is 0, p is 0; and further provided that when m is greater than 0, p is 1; and
one or more other repeat units.

50. The copolymer as recited in Claim 49 wherein said hydroxy containing repeat unit is 0.001 to 30 mole percent of the total repeat units in the copolymer.

51. The copolymer as recited in Claim 50 wherein said hydroxy containing repeat unit is 0.05 to 15 mole percent of the total repeat units in the copolymer.

52. The copolymer as recited in Claim 49 wherein at least one of said other repeat units is derived from a fluoromonomer.

53. The copolymer as recited in Claim 49 wherein the said other repeat unit(s) are derived from monomers selected from the group consisting of tetrafluoroethylene; hexafluoropropylene and vinylidene fluoride; hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene; ethylene and vinylidene fluoride; perfluoro(methyl vinyl ether) and tetrafluoroethylene; perfluoro(methyl vinyl ether) and hexafluoropropylene; chlorotrifluoroethylene; ethylene and chlorotrifluoroethylene; vinylidene fluoride; tetrafluoroethylene and propylene; tetrafluoroethylene and ethylene; tetrafluoroethylene and hexafluoropropylene; perfluoro-2,2-dimethyl-1,3-dioxole; perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene; vinyl fluoride; tetrafluoroethylene and perfluoro[2-(2-fluorosulfonylethoxy)propyl vinyl ether]; and vinyl acetate and tetrafluoroethylene.

54. The copolymer as recited in Claim 49 wherein at least one of said other repeat units is derived from a vinyl ester.

55. The copolymer as recited in Claim 54 wherein said vinyl ester is vinyl acetate.

56. The copolymer as recited in Claim 49 wherein said other repeat units are derived from vinyl acetate and tetrafluoroethylene.

Patentansprüche

1. Verfahren zur Herstellung hydroxyhaltiger Fluorvinylverbindungen, umfassend das Bringen eines Alkalimetallborhydrids in einem Lösungsmittel in Kontakt mit einer Verbindung der Formel $CF_2 = CFR^1CO_2R^2$,

worin:

R^1 aus einer kovalenten Bindung, einer Perfluoralkylengruppe und $-OR^3-$ ausgewählt wird,
R^2 ein Kohlenwasserstoff- oder substituierter Kohlenwasserstoffrest ist und
R^3 eine Perfluoralkylengruppe ist,

wobei "Perfluoralkylengruppe" bei R^1 und R^3 ein zweiwertiger gesättigter Rest ist, der durch Entfernung von zwei Fluoratomen von verschiedenen Kohlenstoffatomen von einem perfluorierten Alkan

abgeleitet ist und gegebenenfalls Sauerstoffatome, zwischen Segmenten enthält, so daß in jeder Perfluoralkylengruppe eine oder mehrere Ethergruppen gebildet werden.

2. Verfahren gemäß Anspruch 1, wobei das Lösungsmittel ein Alkohol ist.

3. Verfahren gemäß Anspruch 2, wobei der Alkohol aus der Gruppe ausgewählt wird, die aus Ethanol und Methanol besteht.

4. Verfahren gemäß Anspruch 1 oder 2, wobei die Temperatur -10 ° bis +30 ° C beträgt.

5. Verfahren gemäß Anspruch 4, wobei die Temperatur 0 ° bis 15 ° C beträgt.

6. Verfahren gemäß Anspruch 5, wobei die Temperatur 5 ° bis 10 ° C beträgt.

7. Verfahren gemäß Anspruch 1 oder 2, wobei das Stoffmengenverhältnis des Borhydrids zu der genannten Verbindung 0,3 bis etwa 1,2 beträgt.

8. Verfahren gemäß Anspruch 7, wobei das Stoffmengenverhältnis 0,4 bis 0,8 beträgt.

9. Verfahren gemäß Anspruch 1 oder 2, wobei die Reaktionsmasse gerührt wird.

10. Verfahren gemäß Anspruch 1, wobei R^1 $-OR^3-$ ist, wobei R^3 $-(CF_2)_y-$ ist, wobei y 2 bis 10 beträgt.

11. Verfahren gemäß Anspruch 1, wobei R^1 $-OR^3-$ ist, wobei R^3 $-[CF_2CF(CF_3)O]_x(CF_2)_z-$ ist, wobei z 1 bis 10 beträgt und x 1 bis 20 beträgt.

12. Verfahren gemäß Anspruch 11, wobei x 1 ist und z 2 ist.

13. Verfahren gemäß Anspruch 1, wobei R^1 Perfluoralkylen ist.

14. Verfahren gemäß Anspruch 13, wobei R^1 $-(CF_2)_q-$ ist, wobei q 1 bis 10 beträgt.

15. Verfahren gemäß Anspruch 1, wobei R^1 eine kovalente Bindung ist.

16. Verfahren gemäß Anspruch 1, 2, 10, 11, 12, 13, 14 oder 15, wobei R^2 Alkyl ist.

17. Verfahren gemäß Anspruch 1 oder 2, wobei das Alkalimetallborhydrid aus der Gruppe ausgewählt wird, die aus Lithiumborhydrid, Natriumborhydrid und Kaliumborhydrid besteht.

18. Verfahren gemäß Anspruch 7, wobei die Temperatur -10 ° bis +30 ° C beträgt.

19. Hydroxyhaltige Fluorvinylether der Formel $CF_2=CF[OCF_2CF(CF_3)]_n(O)_p(CF_2)_mCH_2OH$, worin:
p 0 oder 1 ist,
m 0 bis 10 beträgt und n 1 bis 20 beträgt,
mit der Maßgabe, daß p 0 ist, wenn m 0 ist, und mit der weiteren Maßgabe, daß p 1 ist, wenn m größer als 0 ist.

20. Ether gemäß Anspruch 19, wobei:
n 1 bis 5 beträgt,
p 1 ist und
m 2 bis 10 beträgt.

21. Ether gemäß Anspruch 19, wobei:
n 1 ist,
p 1 ist und
m 2 ist.

22. Verfahren zum Polymerisieren hydroxyhaltiger Fluorvinylether, umfassend das Bringen einer Base in Kontakt mit einem oder mehreren Hydroxyfluorvinylethern der Formel $CF_2=CFOR^4CF_2CH_2OH$, worin R^4 Perfluoralkylen ist.

23. Verfahren gemäß Anspruch 22, das in einem Lösungsmittel durchgeführt wird.

24. Verfahren gemäß Anspruch 23, wobei das Lösungsmittel ein polares, aprotisches Lösungsmittel ist.

25. Verfahren gemäß Anspruch 24, wobei das Lösungsmittel aus der Gruppe ausgewählt wird, die aus N,N-Dimethylformamid, Dimethylsulfoxid, N,N-Dimethylacetamid und Tetrahydrofuran besteht.

26. Verfahren gemäß Anspruch 25, wobei es sich bei dem Lösungsmittel um N,N-Dimethylformamid handelt.

27. Verfahren gemäß Anspruch 22 oder 24, wobei die Base aus der Gruppe ausgewählt wird, die aus Alkalimetallalkoxiden, Alkalimetallhydriden und Aminen besteht.

28. Verfahren gemäß Anspruch 27, wobei die Base ein Alkalimetallalkoxid ist.

29. Verfahren gemäß Anspruch 28, wobei es sich bei dem Alkalimetallalkoxid um Kalium-t-butoxid handelt.

30. Verfahren gemäß Anspruch 22 oder 24, wobei die Temperatur -10° bis +100°C beträgt.

31. Verfahren gemäß Anspruch 30, wobei die Temperatur 0° bis 50°C beträgt.

32. Verfahren gemäß Anspruch 31, wobei die Temperatur 10° bis 30°C beträgt.

33. Verfahren gemäß Anspruch 22, 24 oder 27, wobei das Stoffmengenverhältnis des hydroxyhaltigen Fluorvinylethers zu der Base 5 bis 100 beträgt.

34. Verfahren gemäß Anspruch 33, wobei das Stoffmengenverhältnis 8 bis 50 beträgt.

35. Verfahren gemäß Anspruch 34, wobei das Stoffmengenverhältnis 10 bis 25 beträgt.

36. Verfahren gemäß Anspruch 22 oder 24, wobei die Reaktionsmasse gerührt wird.

37. Verfahren gemäß Anspruch 24, wobei R^4 $-(CF_2)_s-$ ist, wobei s 1 bis 10 beträgt.

38. Verfahren gemäß Anspruch 37, wobei s 2 ist.

39. Verfahren gemäß Anspruch 24, wobei R^4 $-[CF_2CF(CF_3)O]_t(CF_2)_u-$ist, wobei u 1 bis 10 beträgt und t 1 bis 20 beträgt.

40. Verfahren gemäß Anspruch 39, wobei t 1 ist und u 1 ist.

41. Verfahren gemäß Anspruch 37 oder 39, wobei die Temperatur -10° bis +100°C beträgt.

42. Verfahren gemäß Anspruch 40 oder 41, wobei das Stoffmengenverhältnis des hydroxyhaltigen Fluorvinylethers zu der Base 5 bis 100 beträgt.

43. Verfahren gemäß Anspruch 42, wobei die Base ein Alkalimetallalkoxid ist.

44. Polymer, das im wesentlichen aus der Repetiereinheit der Formel $-[CF_2CFHOR^4CF_2CH_2O]-$ besteht, worin R^4 Perfluoralkylen ist.

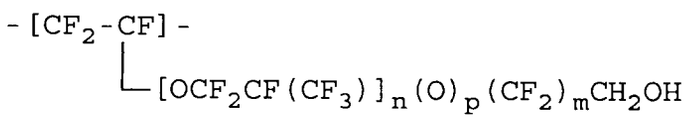
45. Polymer gemäß Anspruch 44, wobei R^4 $-(CF_2)_s-$ ist, wobei s 1 bis 10 beträgt.

46. Polymer gemäß Anspruch 45, wobei s 2 ist.

47. Polymer gemäß Anspruch 44, wobei R^4 -$[CF_2CF(CF_3)O]_t(CF_2)_u$-ist, wobei t 1 bis 20 beträgt und u 1 bis 10 beträgt.

48. Polymer gemäß Anspruch 47, wobei t 1 ist und u 1 ist.

49. Copolymer, das die hydroxyhaltige Repetiereinheit



worin:

p 0 oder 1 ist,

m 0 bis 10 beträgt und

n 1 bis 20 beträgt,

mit der Maßgabe, daß p 0 ist, wenn m 0 ist, und mit der weiteren Maßgabe, daß p 1 ist, wenn m größer als 0 ist,

sowie eine oder mehrere weitere Repetiereinheiten umfaßt.

50. Copolymer gemäß Anspruch 49, wobei die hydroxyhaltige Repetiereinheit 0,001 bis 30 Molprozent der gesamten Repetiereinheiten in dem Copolymer ausmacht.

51. Copolymer gemäß Anspruch 50, wobei die hydroxyhaltige Repetiereinheit 0,05 bis 15 Molprozent der gesamten Repetiereinheiten in dem Copolymer ausmacht.

52. Copolymer gemäß Anspruch 49, wobei wenigstens eine der weiteren Repetiereinheiten von einem Fluormonomer abgeleitet ist.

53. Copolymer gemäß Anspruch 49, wobei die weitere(n) Repetiereinheit(en) von Monomeren abgeleitet ist (sind), die aus der Gruppe ausgewählt sind, bestehend aus: Tetrafluorethylen; Hexafluorpropylen und Vinylidenfluorid; Hexafluorpropylen, Vinylidenfluorid und Tetrafluorethylen; Ethylen und Vinylidenfluorid; Perfluor(methylvinylether) und Tetrafluorethylen; Perfluor(methylvinylether) und Hexafluorpropylen; Chlortrifluorethylen; Ethylen und Chlortrifluorethylen; Vinylidenfluorid; Tetrafluorethylen und Propylen; Tetrafluorethylen und Ethylen; Tetrafluorethylen und Hexafluorpropylen; Perfluor-2,2-dimethyl-1,3-dioxol; Perfluor2,2-dimethyl-1,3-dioxol und Tetrafluorethylen; Vinylfluorid; Tetrafluorethylen und Perfluor[2-(2-fluorsulfonylethoxy)propylvinylether]; sowie Vinylacetat und Tetrafluorethylen.

54. Copolymer gemäß Anspruch 49, wobei wenigstens eine der weiteren Repetiereinheiten von einem Vinylester abgeleitet ist.

55. Copolymer gemäß Anspruch 54, wobei es sich bei dem Vinylester um Vinylacetat handelt.

56. Copolymer gemäß Anspruch 49, wobei die weiteren Repetiereinheiten von Vinylacetat und Tetrafluorethylen abgeleitet sind.

Revendications

1. Un procédé pour la production de composés fluorovinyliques hydroxylés comprenant la mise en contact dans un solvant d'un borohydrure de métal alcalin avec un composé de formule $CF_2 = CFR^1CO_2R^2$,

où : R^1 est choisi parmi une liaison covalente, un groupe perfluoroalkylène et un groupe -OR^3- ;

R^2 est un groupe hydrocarbyle ou un groupe hydrocarbyle substitué ; et

R^3 est un groupe perfluoroalkylène,

le "groupe perfluoroalkylène" de R^1 et R^3 étant un radical saturé bivalent dérivant d'un alcane perfluoré par enlèvement de deux atomes de fluor à deux atomes de carbone différents et qui contient facultativement des atomes d'oxygène séparant des segments pour former un ou plusieurs groupes

éther dans chaque groupe perfluoroalkylène.

2. Le procédé énoncé dans la revendication 1 dans lequel ledit solvant est un alcool.

3. Le procédé énoncé dans la revendication 2 dans lequel ledit alcool est choisi dans le groupe formé par l'éthanol et le méthanol.

4. Le procédé énoncé dans la revendication 1 ou la revendication 2 dans lequel la température est de -10 à +30 °C.

5. Le procédé énoncé dans la revendication 4 dans lequel ladite température est de 0 à 15 °C.

6. Le procédé énoncé dans la revendication 5 dans lequel ladite température est de 5 à 10 °C.

7. Le procédé énoncé dans la revendication 1 ou la revendication 2 dans lequel le rapport molaire dudit borohydrure audit composé est de 0,3 à environ 1,2.

8. Le procédé énoncé dans la revendication 7 dans lequel ledit rapport molaire est de 0,4 à 0,8.

9. Le procédé énoncé dans revendication 1 ou la revendication 2 dans lequel la masse réactionnelle est agitée.

10. Le procédé énoncé dans la revendication 1 dans lequel R^1 est $-OR^3-$, où R^3 est $-(CF_2)_y-$, avec y valant 2 à 10.

11. Le procédé énoncé dans la revendication 1 dans lequel ledit R^1 est $-OR^3-$, où R^3 est $-[CF_2CF(CF_3)O]_x-(CF_2)_z-$, avec z valant 1 à 10 et x valant 1 à 20.

12. Le procédé énoncé dans la revendication 11 dans lequel ledit x vaut 1 et ledit z vaut 2.

13. Le procédé énoncé dans la revendication 1 dans lequel ledit R^1 est un groupe perfluoroalkylène.

14. Le procédé énoncé dans la revendication 13 dans lequel ledit R^1 est un groupe $-(CF_2)_q$, où q vaut 1 à 10.

15. Le procédé énoncé dans la revendication 1 dans lequel ledit R^1 est une liaison covalente.

16. Le procédé énoncé dans la revendication 1 ou la revendication 2 ou la revendication 10, ou la revendication 11 ou la revendication 12 ou la revendication 13, ou dans la revendication 14 ou la revendication 15, dans lequel ledit R^2 est un groupe alkyle.

17. Le procédé énoncé dans la revendication 1 ou la revendication 2 dans lequel ledit borohydrure de métal alcalin est choisi dans le groupe formé par le borohydrure de lithium, le borohydrure de sodium et le borohydrure de potassium.

18. Le procédé énoncé dans la revendication 7 dans lequel la temperature est d'environ -10 à environ +30 °C.

19. Ethers fluorovinyliques hydroxylés de formule

$$CF_2=CF[OCF_2CF(CF_3)]_n(O)_p(CF_2)_mCH_2OH,$$

où : p est 0 ou 1 ;
m est 0 à 10 et n est 1 à 20 ; et
si m est 0, p est 0 ; et si en en outre m est supérieur à 0, p est 1.

20. Les éthers définis dans la revendication 19 dans lesquels :
n est 1 à 5 ;

p est 1 ; et
m est 2 à 10.

21. Les éthers définis dans la revendication 19 dans lesquels :
n est 1 ;
p est 1 ; et
m est 2.

22. Un procédé pour polymériser des éthers fluorovinyliques hydroxylés, comprenant la mise en contact d'une base avec un ou plusieurs éthers hydroxy fluorovinyliques de formule $CF_2=CFOR^4CF_2CH_2OH$, Où R^4 est un groupe perfluoroalkylène.

23. Le procédé énoncé dans la revendication 22 mis en oeuvre dans un solvant.

24. Le procédé énoncé dans la revendication 23 dans lequel ledit solvant est un solvant aprotique polaire.

25. Le procédé énoncé dans la revendication 24 dans lequel ledit solvant est choisi dans le groupe formé par le N'N'-diméthylformamide, le diméthylsulfoxyde, le N,N-diméthylacétamide et le tétrahydrofurane.

26. Le procédé énoncé dans la revendication 25 dans lequel ledit solvant est le N,N-diméthylformamide.

27. Le procédé énoncé dans la revendication 22 ou la revendication 24 dans lequel ladite base est choisie dans le groupe formé par les alcoolates de métaux alcalins, les hydrures de métaux alcalins et les amines.

28. Le procédé énoncé dans la revendication 27 dans lequel ladite base est un alcoolate de métal alcalin.

29. Le procédé énoncé dans la revendication 28 dans lequel ledit alcoolate de métal alcalin est le tert-butylate de potassium.

30. Le procédé énoncé dans la revendication 22 ou la revendication 24 dans lequel la température est de -10 à +100 °C.

31. Le procédé énoncé dans la revendication 30 dans lequel ladite température est de 0 à 50 °C.

32. Le procédé énoncé dans la revendication 31 dans lequel ladite température est de 10 à 30 °C.

33. Le procédé énoncé dans la revendication 22, la revendication 24 ou la revendication 27 dans lequel le rapport molaire dudit éther fluorovinylique hydroxylé à ladite base est de 5 à 100.

34. Le procédé énoncé dans la revendication 33 dans lequel ledit rapport molaire est de 8 à 50.

35. Le procédé énoncé dans la revendication 34 dans lequel ledit rapport molaire est de 10 à 25.

36. Le procédé énoncé dans la revendication 22 ou la revendication 24 dans lequel la masse réactionnelle est agitée.

37. Le procédé énoncé dans la revendication 24 dans lequel ledit R^4 est un groupe $-(CF_2)_s-$, où s vaut 1 à 10.

38. Le procédé énoncé dans la revendication 37 dans lequel ledit s vaut 2.

39. Le procédé énoncé dans la revendication 24 dans lequel ledit groupe R^4 est $-[CF_2CF(CF_3)O]_t(CF_2)_u-$, avec u valant 1 à 10 et t valant 1 à 20.

40. Le procédé énoncé dans la revendication 39 dans lequel ledit t vaut 1 et ledit u vaut 1.

41. Le procédé énoncé dans la revendication 37 ou la revendication 39 dans lequel la température est de -10 à +100 °C.

42. Le procédé énoncé dans la revendication 40 ou la revendication 41 dans lequel le rapport molaire dudit éther fluorovinylique hydroxylé à ladite base est de 5 à 100.

43. Le procédé énoncé dans la revendication 42 dans lequel ladite base est un alcoolate de métal alcalin.

44. Un polymère constitué essentiellement par répétition de la formule $-[CF_2CFHOR^4CF_2CH_2O]-$, où R^4 est un groupe perfluoroalkylène.

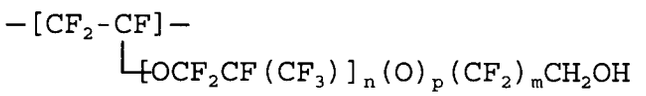
45. Un polymère selon la revendication 44 dans lequel ledit groupe R^4 est $-(CF_2)_s-$, où s vaut 1 à 10.

46. Le polymère selon la revendication 45 dans lequel ledit s vaut 2.

47. Un polymère selon la revendication 44 dans lequel ledit groupe R^4 est $-[CF_2CF(CF_3)O]_t(CF_2)_u-$, avec t valant 1 à 20 et u valant 1 à 10.

48. Un polymère selon la revendication 47 dans lequel ledit t vaut 1 et ledit u vaut 1.

49. Un copolymère comprenant le motif répétitif hydroxylé



où :
p est 0 ou 1 ;
m est 0 à 10 ; et
n est 1 à 20 ;
si m est 0, p est 0 ; et
si en en outre m est supérieur à 0, p est 1 ; et
un ou plusieurs autres motifs répétitifs.

50. Le copolymère de la revendication 47 dans lequel ledit motif répétitif hydroxylé constitue 0,001 à 30 moles pour cent du total des motifs répétitifs présents dans le copolymère.

51. Le copolymère de la revendication 50 dans lequel ledit motif répétitif hydroxylé constitue 0,05 à 15 moles pour cent du total des motifs répétitifs présents dans le copolymère.

52. Le copolymère de la revendication 47 dans lequel le ou lesdits plusieurs autres motifs répétitifs dérivent d'un monomère fluoré.

53. Le copolymère de la revendication 49 dans lequel le ou lesdits autres motifs répétitifs dérivent de monomères choisis dans le groupe formé par le tétrafluoréthylène ; l'hexafluoropropylène et le fluorure de vinylidène ; l'hexafluoropropylène, le fluorure de vinylidène et le tétrafluoréthylène ; l'éthylène et le fluorure de vinylidène ; le perfluoro(oxyde de méthyle et de vinyle) et le tétrafluoréthylène ; le perfluoro(oxyde de méthyle et de vinyle) et l'hexafluoropropylène ; le chlorotrifluoréthylène ; l'éthylène et le chlorotrifluoréthylène; le fluorure de vinylidène ; le tétrafluoréthylène et le propylène ; le tétrafluoréthylène et l'éthylène ; le tétrafluoréthylène et l'hexafluoropropylène ; le perfluoro-2,2-diméthyl-1,3-dioxole ; le perfluoro-2,2-diméthyl-1,3-dioxole et le tétrafluoréthylène ; le fluorure de vinyle ; le tétrafluoréthylène et le perfluoro[oxyde de 2-(2-fluorosulfonyléthoxy)propyle et de vinyle] ; et l'acétate de vinyle et le tétrafluoréthylène.

54. Le copolymère de la revendication 49 dans lequel l'un au moins desdits autres motifs répétitifs dérive d'un ester vinylique.

55. Le copolymère de la revendication 54 dans lequel ledit ester vinylique est l'acétate de vinyle.

56. Le copolymère de la revendication 47 dans lequel lesdits autres motifs répétitifs dérivent de l'acétate de vinyle et du tétrafluoréthylène.